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Sludge Treatment Studies

E. C. Beahm
C. F. Weber
T. A. Dillow
S. A. Bush
S. Y. Lee
R. D. Hunt

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Chemical Technology Division

SLUDGE TREATMENT STUDIES

E. C. Beahm, C. F. Weber, T. A. Dillow, S. A. Bush,
S. Y. Lee, and R. D. Hunt

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OAK RIDGE NATIONAL LABORATORY
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SUMMARY

A number of similarities exist between Enhanced Sludge Washing and the Bayer process used in the aluminum industry. In the Bayer process, a bauxite slurry is leached with caustic to dissolve alumina from the ore. The goal is to produce alumina in the form of gibbsite, $\text{Al}(\text{OH})_3$. This is done by controlled precipitation. It is very important to control solid formation in Enhanced Sludge Washing as well. Failure to do so will result in the formation of crystalline solids and gels, which are unacceptable because they will (1) prevent mixing; (2) prevent pumping; (3) retard separations; (4) coat surfaces; and (5) clog pipes, equipment, and filters.

Solid formation in filtered leachates and wash solutions was seen in five of the six sludges treated by Enhanced Sludge Washing. Solid formation in process solutions takes a variety of forms: very fine particles, larger particulate solids, solids floating in solution like egg whites, gels, crystals, and coatings on sample containers. A gel-like material that formed in a filtered leachate from Enhanced Sludge Washing of Hanford T-104 sludge was identified as natrophosphate, $\text{Na}_7(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$. A particulate material that formed in a filtered caustic leachate from Hanford SX-113 sludge contained sodium and silicon. This could be any of a host of sodium silicates in the $\text{NaOH-SiO}_2\text{-H}_2\text{O}$ system.

Acidic treatment of Hanford B-202 sludge with 1 M, 3 M, and 6 M HNO_3 sequential leaching resulted in complete dissolution at 75°C , but not at ambient temperature. This treatment resulted in the formation of solids in filtered leachates. Analyses of the solids revealed that a gel material contained silica with some potassium, calcium, iron, and manganese. Two phases were embedded in the gel. One was barium sulfate. The other could not be identified, but it was determined that the only metal it contained was bismuth.

SLUDGE TREATMENT STUDIES

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1. INTRODUCTION

Sludge pretreatment will likely involve washing, followed by caustic or acidic leaching and washing of sludge residues after leaching. The principal goal of pretreatment is to obtain a low-volume high-activity waste stream and a high-volume low-activity waste stream. Also, some waste constituents such as chromium and phosphate can be included in glass formulations only at very low concentrations, so it is desirable to remove them from high-level waste streams.

Two aspects of sludge treatment and subsequent separations should be well delineated and predictable: (1) the distribution of chemical species between aqueous solutions and solids and (2) potential problems due to chemical interactions that could result in process difficulties or safety concerns. Before any treatment technology is adopted, it must be demonstrated that the process can be carried out as planned. Three pretreatment methods were considered in the Tri-Party (Washington State Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy) negotiations: (1) sludge washing with corrosion-inhibiting water, (2) Enhanced Sludge Washing, and (3) acidic dissolution with separations processes. Enhanced Sludge Washing is the baseline process.

In Enhanced Sludge Washing, sludge is first washed with corrosion-inhibiting water; it is then leached with caustic (sodium hydroxide solution) and washed again with corrosion-inhibiting water.

The initial concern is whether a pretreatment technique is effective in separating sludge components. This can be evaluated by bench-scale tests with sludge specimens from underground storage tanks. The results give data on the distribution of important species such as aluminum, phosphate, and radionuclides between wash and leach solutions and solid sludge residues. In addition to tests with sludges, similarities between treatment of underground storage tank sludge and other well-known chemical processes provide insight into sludge pretreatment. The closest parallel to Enhanced Sludge Washing is the Bayer process, which is used in the aluminum industry to separate aluminum oxide from ore. Acidic sludge treatment is similar to many of the leaching processes used in hydrometallurgical winning of metals from ores.

2. ENHANCED SLUDGE WASHING

2.1 ENHANCED SLUDGE WASHING AND THE BAYER PROCESS

It is very important to assess implementation of a pretreatment process. Failure to do so will result in process operating parameters and unit operations that are not well matched to chemical and physical changes that are actually occurring. This assessment requires an evaluation of the overall process, not simply the distribution of species between solids and liquids. Figure 1 shows a simplified diagram of Enhanced Sludge Washing and the Bayer process. In the Bayer process a bauxite slurry is leached with caustic to dissolve alumina from the ore. The goal is to produce alumina in the form of gibbsite, $\text{Al}(\text{OH})_3$. This process has been used for more than 100 years, and the continuous changes it has undergone as new technologies become available make it an excellent starting point for evaluating Enhanced Sludge Washing and for avoiding potential problems.

The Bayer process is similar to Enhanced Sludge Washing. First, the material being treated, either sludge or bauxite, is digested at some temperature (T_1 in Fig. 1) by a caustic solution. This is followed by a solid-liquid separation at a temperature $T_2 \leq T_1$. The solids are then washed, and another solid-liquid separation takes place. The liquid from digestion and washing is combined at a temperature $T_3 \leq T_2$. In the Bayer process, controlled precipitation of gibbsite occurs at this point. It is very important in these processes to prevent formation of solids by uncontrolled precipitation (autoprecipitation). Failure to do so will result in the formation of crystalline solids and gels, which are unacceptable because they will (1) prevent mixing; (2) prevent pumping; (3) retard separations; (4) coat surfaces; and (5) clog pipes, equipment, and filters.

A number of techniques can be used to control the formation of solids. First, complete dissolution of materials that can reprecipitate reduces the possibility of autoprecipitation because no seed crystals remain in the solids to induce precipitation. This technique is used in the Bayer process, in which almost 100% of the alumina is dissolved during digestion. Second, temperatures can be maintained in the process to prevent solids formation that occurs when wash solutions or leachates that are at or near saturation are cooled. After digestion at temperature T_1 , either of two things can

Fig. 1. Simplified diagram of Enhanced Sludge Washing and the Bayer process.

happen if the temperature decreases, assuming that the leachate is at or near saturation in at least one species: (1) reprecipitation back to the sludge solids or (2) supersaturation of the leachate. Supersaturation is a metastable state that can result in reprecipitation elsewhere in the process. Thus, in either case, allowing the system to cool after digestion and before solid-liquid separation leads to an undesirable result. If the material reprecipitated is a major component such as alumina, the heating during digestion enhances only the rate that the saturated concentration referred to ambient temperature is reached, not the amount of material ultimately in solution.

In the third option for controlling solid formation, excess caustic is used to avoid exceeding solubility limits, even when the solutions are cooled or when leachates and wash solutions are mixed. In addition to these three techniques, controlled precipitation, as in the Bayer process, may improve process control. Of course, in the Bayer process, controlled precipitation is used to obtain the gibbsite product. In Enhanced Sludge Washing the combination of leachate and wash solutions occurs in a wash accumulation tank rather than in the controlled precipitation portion, as in the Bayer process. Clearly if some of the three techniques for controlling solids formation in Enhanced Sludge Washing are not in place, precipitation is likely in the wash accumulation tank or in associated piping.

The relation between temperature, concentration, and precipitation can be illustrated by considering phase diagrams applicable to alumina dissolution, shown in Fig. 2. This figure shows the phases in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system at 30°C and at 95°C .¹ The areas enclosed by lines connecting points a, b, and c and those connecting a', b', and c', respectively, are the solution fields, which denote the limits of solubility. This field is larger in the 95°C phase diagram (a', b', c' area) than in the 30°C phase diagram (a, b, c area). This reflects greater solubility at the higher temperature.

The lines a'b' and b'c' in the 95°C diagram give the saturated solution limits. Thus, point b' corresponds to a saturated solution at 95°C . Point d' in the 95°C diagram and point d in the 30°C diagram have the same $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ composition. However, point d' is in a liquid solution region, whereas point d (at the lower temperature) is in a region that contains solid $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ in addition to saturated solution. This illustrates what will occur when a saturated or near-saturated solution is cooled and equilibrium is maintained. If the system does not reach equilibrium, the

Fig. 2. Phase diagrams of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at (a) 30°C and (b) 95°C.

composition represented by point d would be supersaturated with respect to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and solid formation may occur elsewhere in the process whether it is desired or not.

Solids may also form as a result of sludge washing or mixing of wash solutions and leachates. This results from dilution of the caustic. In Fig. 2(a), point e is on the saturated solution line. A straight line drawn from point e to point a crosses the region where both solid $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and saturated solution are present. This represents simply adding water (approaching point a) to a saturated solution (represented by point e). The same thing occurs when any saturated or near-saturated solution encounters wash water (point e was randomly selected). With reference to Fig. 1, this could occur in the "water" wash or when liquid from digestion meets liquid from wash.

2.2 THERMODYNAMIC CALCULATIONS

Phase diagrams are useful for describing what is possible in a process; however, thermochemical calculations on specific sludge material are better for determining the equilibrium dissolution and precipitation behavior. Equilibrium calculations of alumina behavior in Enhanced Sludge Washing of Hanford S-104 and T-104 sludge were carried out. Details of the calculational method and thermochemical data are given in Reference 2. For this series of calculations, the species set included H_2O , Na^+ , OH^- , H^+ , $\text{Al}(\text{OH})_4^-$, AlOOH , $\text{Al}(\text{OH})_3$, and NaNO_3 .

2.2.1 Precipitation of Alumina

Two different scenarios involving S-104 sludge were evaluated: (1) leaching at 75°C or 100°C, cooling to 25°C before solid-liquid separation, and washing at 25°C, or (2) leaching at 75°C or 100°C, solid-liquid separation at 75°C or 100°C, and washing at 25°C. Figure 3 plots the equilibrium calculation of alumina precipitation back to the sludge solids residue after leaching at 75°C or 100°C and cooling to 25°C. In this figure "Original Net Dissolved" is the percentage of alumina in the S-104 sludge that was dissolved during leaching, and "Reprecipitated in Residue" is the percentage of the Original Net Dissolved that would reprecipitate after cooling to 25°C.

Fig. 3. Equilibrium calculation of alumina precipitation back to residue: S-104 sludge; 3 m NaOH; digestion temperature, 75°C or 100°C; decantation of leach after cooling to 25°C.

For example, a leachate at 75°C that resulted in 62% dissolution of alumina would reprecipitate ~38% of the dissolved material on cooling to 25°C. Figure 4 plots the equilibrium alumina precipitation in the combined leach and wash solutions that follow the leachate depicted in Fig. 3. In this case, the percentage of the original dissolved material that reprecipitates is on the order of 1 to 3%. This results from dilution of caustic leachate by the water wash.

Figures 5 and 6 illustrate the calculated equilibrium behavior of alumina when both leaching and solid-liquid separation are performed at 75°C or 100°C. Figure 5 shows plots of reprecipitation to the residue. This 1 to 3% reprecipitation resulted from dilution of the caustic leachate that remained with the residue by the water wash. Figure 6 shows plots of alumina precipitation in combined leach and wash solutions. Most of this precipitation resulted from the temperature decrease from 75°C or 100°C to 25°C.

Fig. 4. Equilibrium calculation of alumina precipitation in combined leach and wash solutions: S-104 sludge; 3 *m* NaOH, digestion temperature, 75°C or 100°C; decantation of leach after cooling to 25°C.

Fig. 5. Equilibrium calculation of precipitation in residue: S-104 sludge, 3 *m* NaOH, digestion and decantation of leach at 75°C or 100°C, wash at 25°C.

Fig. 6. Equilibrium calculation of alumina precipitation in combined leach and wash solutions: S-104 sludge, 3 *m* NaOH, digestion and decantation of leach at 75°C or 100°C, wash at 25°C.

2.2.2 Excess Caustic and Caustic Consumption

The calculations on S-104 sludge are described first. The caustic solution was chosen so that the resulting solution at equilibrium was exactly 3 molal (*m*) in hydroxide (OH^-). The initial concentration required was $3.1 < m < 3.8$. In Fig. 7 caustic leaching is represented as a function of liters of caustic per kilogram of aluminum (L/kg Al). The line labeled "Undissolved in Sludge" gives the percentage of undissolved aluminum as a function of (L/kg Al). The percentage of undissolved aluminum reaches zero at an (L/kg Al) of about 75. This is also the point at which the percentage of aluminum precipitated back to the leachate reaches its maximum. In addition, a relatively small amount of aluminum would reprecipitate back to the sludge residue. (Note: This curve is 10 times the calculated percentage.) At (L/kg Al) values ≥ 75 , the percentage of aluminum precipitated in the leachate or reprecipitated in residue decreases and becomes zero at ~ 200 . If the sludge were leached at 100°C instead of 75°C, the percentage of aluminum "Undissolved in Sludge" would reach zero at an (L/kg Al) of ~ 48 rather than ~ 75 . This phenomenon results from the greater solubility of

Fig. 7. Calculation of S-104 caustic leaching at 75°C: sufficient caustic added so that mixture is 3 *m* OH⁻; ambient temperature, 25°C.

alumina at the higher temperature. However, the (L/kg Al) where no aluminum precipitated in the leachate or reprecipitated in the residue would be similar in both cases because the ambient temperature of 25°C was the same and the same amount of aluminum was involved in the process.

It should be emphasized that only a fraction of the caustic would be consumed in the reaction with alumina:

Most of the caustic indicated in the large (L/kg Al) values would be needed to maintain the OH⁻ concentration in saturated alumina solutions or would be the excess necessary to prevent precipitation when the temperature is lowered or when leachates and wash solutions are mixed.

Other materials in sludge such as silicates, acid phosphates, and perhaps zirconia can also consume caustic. The T-104 sludge contains a relatively high concentration of phosphorus and has a pH of ~ 10.5 . At this pH the phosphate would be HPO_4^{-2} . In caustic leaching this would consume OH^- and convert to phosphate PO_4^{-3} :

This effect was seen experimentally in a test in which the final caustic concentration could be related to the amount consumed by both aluminum and acid phosphate. This is shown in the calculations represented by Fig. 8. In these calculations the initial sodium hydroxide concentration was 3 molal (m). The final caustic concentration was $\sim 2.1 m$, due to consumption of caustic by aluminum and acid phosphate. In Fig. 8 the slope of the line "Undissolved in Sludge" is initially somewhat flat because the caustic is being consumed in the conversion of acid phosphate to phosphate. With the addition of more caustic, the percentage of aluminum undissolved in sludge decreases more rapidly. The (L/kg Al) at the point at which the percentage precipitated in leachate or reprecipitated in sludge approaches zero is again ~ 200 .

In the *Status Report: Pretreatment Chemistry Evaluation – Wash and Leach Factors for the Single-Shell Tank Waste Inventory*,³ N. G. Colton gives the expected inventories of aluminum and sodium in Hanford single-shell tanks as 6,280 metric tons and 43,000 metric tons, respectively. If 200 (L/kg Al) is used as the estimated caustic-to-aluminum ratio needed to avoid precipitation in solutions or residues, then $\sim 1 \times 10^9$ L of $\sim 3 m$ sodium hydroxide is indicated. This would contain twice the amount of sodium presently in the single-shell tanks.

2.3 LABORATORY STUDIES

Enhanced Sludge Washing tests were performed on sludge from Hanford underground storage tanks T-104, S-104, C-105, C-107, C-108, and SX-113 to evaluate the formation of solids in leachates and wash solutions and the treatability of these materials by caustic processing. The test sequences were similar to the process shown in Fig. 1. Thus, the sludge samples, 2–10 g, were

Fig. 8. Calculation of T-104 caustic leaching: OH^- , initially 3 *m* at 75°C; ambient temperature, 25°C.

leached at temperature T_1 , and the solid-liquid separation was carried out at T_2 . The sludge solids were then washed and another solid-liquid separation was performed. After the test the leachates and wash solutions were examined for solid formation and chemical composition. The samples were filtered through 0.45- μm Teflon syringe filters. In the tests in which filtration was done at a temperature above ambient, the filter and syringe were preheated. The tests were run in high-density polyethylene containers, and leachates and wash solutions were placed in clear polystyrene tubes for observation.

A Hach 2100 AN turbidimeter was used to measure turbidity in the leachates and wash solutions. This instrument is capable of reading from 0–10,000 nephelometric turbidity units (NTU). This instrument is checked weekly with a GELEX standard (metal oxide suspended in a gel). The sample solutions were also visually examined for the formation of solids.

These tests demonstrated that solid formation in process solutions takes a variety of forms: very fine particles, larger particulate solids, solids floating in solution like egg whites, gels, crystals, and coatings on sample containers. Solid formation has been seen in wash solutions before and after leaching as well as in leachates. Colloids appeared in the second wash (0.01 *M* NaOH +

0.01 M NaNO_2) before caustic leaching of Hanford T-104 sludge (30 wt % solids). The sludge was washed twice (4 g wash solution/g of initial sludge) at ambient temperature. No solids were seen in the first wash solution. The ionic strength of the first wash solution was 0.45, and the ionic strength of the second wash solution was 0.1. In this same test sequence, a gel formed in the second wash after leaching with 3 M NaOH . The ionic strength of the second wash after leaching was 0.07.

Two test sequences were conducted on sludge from T-104 under conditions that were identical except for the temperature. The treatments started with a wash with inhibited water (0.01 M NaOH + 0.01 M NaNO_2). After the liquid was centrifuged and decanted, the sludge was leached with 3 M NaOH and centrifuged; the leachate was then decanted. The sludge was next leached with 3 M NaOH , centrifuged, and decanted. The treatment concluded with three washes with inhibited water, with centrifugation and decantation after each wash. The initial wash and the two leaches were carried out at 60°C in one test sequence and at 95°C in the other test sequence. The centrifugation, filtration, decantation, and the three washes after leaching were performed at ambient temperature.

One day after leaching, gels were observed in both the first and second leachates from both test sequences. A sample of the gel that formed in this sequence was examined by X-ray diffraction and scanning electron microscopy. Figure 9 shows the X-ray diffraction pattern and the identification of the material as natrophosphate, $\text{Na}_7(\text{PO}_4)_2\text{F} \cdot 19\text{H}_2\text{O}$. When this substance was wet, it looked like a gel; it was soft and stuck to the sample container walls. When it was dried, it appeared as a white mass. Scanning electron microscope photographs of the dried material showed groups of crystals (Fig. 10). Chemical analysis of the gel gave the relative moles as 7 sodium, 2.2 phosphate, and 0.93 fluoride and indicated a trace of potassium and sulfate. This is close to the ratios from X-ray diffraction. It is noteworthy that there was very little aluminum in the gel. The sodium-to-aluminum ratio was 4×10^4 even though the leachate in contact with the gel had an aluminum concentration of 0.2 M .

Two test sequences were carried out on sludge from Hanford underground storage tank T-104 to evaluate the behavior of phosphate. In one test sequence the temperature was 75°C throughout all steps of the process. In the other test sequence, the 75°C temperature was maintained only during leaching; after that time, the process was carried out at room temperature. The two processes were carried out in parallel to ensure that temperature was the only variable.

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Fig. 9. X-ray diffraction pattern and identification of dry gel: T-104 sludge, 3.3 M NaOH, 95° treatment.

Fig. 10. Scanning electron microscope photographs of dried gel material: T-104 sludge, 3.3 M NaOH at 95° treatment.

A marked difference in the behavior of phosphate was observed in the two tests. In the test in which the leachate was maintained at 75°C during settling and filtration, the amount of phosphate was approximately 10 times greater than in the leachate from the sequence in which the leaching was performed at 75°C and the settling and filtration were conducted at room temperature. This is direct evidence that the phosphate reprecipitated into the sludge residue-leachate mixture when the temperature was reduced to ambient. Because of this reprecipitation more phosphate was observed in the sludge residue after leaching than in the case where temperature was maintained at 75°C. This resulted in higher concentrations in the wash solutions at ambient temperature than in those at 75°C. In the test sequence maintained at 75°C, most of the phosphate remained in the leachate and was not present in the sludge residue at the time of washing.

These results have several implications. First, the temperature of the leachate enhanced the solubility of the phosphate. Second, running the process with leaching at an elevated temperature and the rest of the process at ambient could possibly increase the rate of dissolution of phosphate, but reprecipitation would return the concentration to that consistent with room temperature. The reprecipitated phosphate is rather gelatinous and sticks to container walls. Third, if the leaching temperature is not maintained throughout the process, phosphate solids will form whenever it is lowered.

Enhanced Sludge Washing tests have been run with sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solid formation. The C-108 and SX-113 sludge were separately leached with 3 M NaOH and washed three times with inhibited water. The temperature throughout the leaching, settling, washing, and filtration was 75°C. The ratio of leachate or wash solution to sludge weight was 10, based on the original mass of sludge. The C-105 and C-107 sludges were separately leached at 70°C in 6 M NaOH as part of the Sludge Partitioning Chemistry program (3TFA), managed by B. Z. Egan. After leaching, the sludge residue was washed three times at ambient temperature. In the tests with C-108 and SX-113 sludge, the process solutions were first examined for solids ~30 min after filtration. The tests with the material from C-105 and C-107 were run in a hot cell, and a 2-day delay occurred before the first examination could be carried out.

Solids formed in filtered process solutions from each of these sludges. With C-105 and C-107, a clear gel-like material formed in the leachates. Wash solutions from the C-105 and C-107

tests also had some clear masses. The leachate from the C-108 test developed a mass of gel-like material as well as some material that appeared to be more crystalline. The wash solutions from the C-108 test developed a small amount of a filmy fibrous material. The filtered leachate from the SX-113 test produced a significant amount of particulate material, which appeared to be semigelatinous when suspended. Scanning electron microscopy with energy dispersive X-ray analysis showed that these particles contained sodium and silicon. This could be any of a host of sodium silicates in the $\text{NaOH} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ system.

3. ACID TREATMENT

The goal of both Enhanced Sludge Washing and acid treatment is to obtain a low-volume high-activity waste stream and a high-volume low-activity waste stream. Subsequent to dissolution the acidic leachate and wash solutions would be subjected to separations processes such as TRUEX and ion exchange to remove radionuclides. In studies of acid treatment of sludge from Melton Valley Storage Tank W-25, the dissolution of solids ranged from 63 to 82%. The highest dissolution percentage was obtained in a sequential leaching sequence that began with a wash with 0.16 M NaOH and was followed by leaching with 0.5, 3, and 6 M HNO_3 . The residue after the acid treatment looked like sandy soil.

Clay is difficult to dissolve by acidic treatment. Aluminum dissolution from clay has been proposed as an alternative to treatment of bauxite in the Bayer process. In that application the clay was first roasted at ~ 1000 K to make it more soluble in acid. Other methods involving mixed acids have been tried, but no commercial use has been made of any acid treatment technique for aluminum dissolution from clay.

Sludge solids contain silica, aluminum, and a variety of metal ions that may participate in gels if they enter solution during processing. At pH levels ≤ 7 , silica in solution as silicic acid, $\text{Si}(\text{OH})_4$, is stable for long periods of time if the concentration is ≤ 100 ppm. At greater concentrations, silicic acid polymerizes according to the general equation,⁴

where n = the number of silicon atoms in a polysilicic acid molecule or particle or polymeric network, x = the number of OH groups per silicon atom in the polymer (not exceeding 4), m = the number of monomeric silicic acid molecules added to the polymer, and p = the fraction of the hydroxyl groups per monomeric silicic acid molecule that are converted to water during the polymerization reaction. Polymerization of $\text{Si}(\text{OH})_4$ leads to particles or to the formation of gels.

Acidic treatment of sludge from Hanford underground storage tank B-202 was carried out. This material was selected for testing because it contains a relatively high fraction of transition metals in the sludge solids and because Enhanced Sludge Washing tests run at Pacific Northwest National Laboratory and at Los Alamos National Laboratory showed that only a small fraction of aluminum dissolved in caustic treatment. Two test sequences were run with the B-202 sludge. In both sequences the sludge was leached successively with 1 M , 3 M , and 6 M HNO_3 and then washed with water. In one case, the entire sequence was carried out at 75°C; in the other case, it was performed at ambient temperature. This test plan enabled an evaluation of both acid concentration and temperature. Before treatment the sludge looked like a dark shoe polish. The ratio of leachate or wash to sludge weight was 10, based on the original weight of the sludge.

In the sequence performed at 75°C, sludge solids remained after leaching with 1 M and 3 M HNO_3 . However, the sludge was completely dissolved by the 6 M HNO_3 step in the sequence. This was not the case in the sequence at ambient temperature. In that case sludge solids remained at all times. Thus, the temperature difference between 75°C and ambient was the important factor in the complete dissolution of this material.

The leachates and wash solutions were all filtered through 0.45- μm Teflon syringe filters. Solid formation was observed in all of the leachates. This varied from halo-like deposits on the glass sample tubes to gels and particulates. Analyses of the solids revealed that a gel material contained silica with some potassium, calcium, iron, and manganese. Two phases were embedded in the gel. One was barium sulfate. The other could not be identified, but it was determined that the only metal it contained was bismuth. In addition, particles of a reddish precipitate separate from the gel were found to contain bismuth and chromium as the only metals.

4. DISCUSSION

The Appendix contains photographs of four types of solids that formed in Enhanced Sludge Washing or in acid treatment. The four categories are coagulation (resembling suspended egg whites), light precipitation, heavy precipitation, and gels.

4.1 ENHANCED SLUDGE WASHING

Solid formation in filtered leachates and wash solutions was seen in five of the six sludges treated. The gel material was identified as natrophosphate, $\text{Na}_7(\text{PO}_4)_2\text{F} \cdot 19\text{H}_2\text{O}$. A type of solubility product for natrophosphate may be written as

$$\text{solubility product} = C_{\text{Na}^+}^7 \cdot C_{\text{PO}_4^{3-}}^2 \cdot C_{\text{F}^-} \quad (5)$$

where C_{Na^+} , $C_{\text{PO}_4^{3-}}$, and C_{F^-} refer to molar concentrations of the indicated species. Data reported by Guiot⁵ indicate that the solubility product is on the order of 10^{-2} at 20°C and at least two orders of magnitude greater at 80 – 100°C . In Enhanced Sludge Washing, C_{Na^+} would be $>3\text{ M}$. This means that the factor $C_{\text{Na}^+}^7$ in the solubility product would be on the order of 10^3 – 10^4 . Thus, very low concentrations of PO_4^{3-} and F^- are required to reach the solubility product of $\sim 10^{-2}$. In addition, because natrophosphate is much more soluble at high temperatures, only a very small fraction of saturation in the 80 – 100°C temperature range would result in supersaturation or solid formation at 20°C . The brief description given here does not include activity coefficients and thermochemical activities, which are necessary for a comprehensive evaluation. We are conducting a detailed thermochemical evaluation of all data available in the Na_3PO_4 – NaF – H_2O system to determine compositions and temperatures where solid formation can be avoided.

The composition of phosphate fluorides can vary by substitution of hydroxide, OH^- , for fluoride and vice versa. The substitution of F^- for OH^- in apatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is the basis for the use of fluoride toothpaste. The substitution of OH^- for F^- in natrophosphate would extend the range of conditions where solids can form, $\text{Na}_7(\text{PO}_4)_2(\text{F})_x(\text{OH})_{1-x}$.

In addition to thermochemical calculations, experimental studies of Hanford underground storage tank sludge will be run to assess techniques to avoid solid formation, to redissolve solids, and to mitigate gelation. Potassium phosphates may be less of a problem in gelation and solid formation than sodium phosphates. Substituting KOH for NaOH and maintaining the sodium ion activity at a level less than 1 may deter the formation of phosphate solids. Of course, even if KOH performed well in dissolution and prevented the occurrence of solids, it may be a problem downstream in the process in cesium removal or in glass formulations.

Phosphate and fluoride concentrations in solution can be reduced by the addition of lime, CaO, to form calcium phosphates and calcium fluoride. This addition would be a means to avoid gelation, but it could also introduce problems in Enhanced Sludge Washing. If lime is added during retrieval, gelation would likely be prevented throughout processing, but little or no phosphate removal from sludge solids would occur. Also, experience in Enhanced Sludge Washing of Oak Ridge Melton Valley Storage Tank sludge, which contains high calcium concentrations, showed that little aluminum was dissolved. This was most likely due to the formation of calcium aluminum hydrogarnets. Thus, lime treatment would have to occur after leaching, settling, and decantation. It is also possible that lime could also assist in controlled precipitation of alumina.

Alumina reprecipitation can be controlled by temperature, by excess caustic, or by controlled precipitation. At this time the options for controlling alumina are better defined than those involving phosphate solids. Combinations of caustic and temperature that avoid alumina reprecipitation can be delineated. However, the close temperature control and excess caustic may make this approach impractical, and controlled precipitation may be the most viable option. Of course, any methodology for dealing with alumina reprecipitation will have to be compatible with mitigating formation of phosphate gels and sodium silicate precipitates.

4.2 ACID TREATMENT

In solutions at $\text{pH} \leq 9$, silica concentrations >100 ppm ($1.7 \times 10^{-3} M$ as SiO_2) polymerize, form colloidal particles, and gel.⁴ In salt solutions, a "salting out" effect results in even lower silica solubilities. The solubility in 3 M NaNO_3 solutions at 25°C is $\sim 50\%$ that of silica in water.⁶

Weres et al.⁷ described the conversion of dissolved excess silica to colloidal amorphous silica as occurring by the following steps: (1) the formation of silica polymers, (2) the nucleation of silica polymers to form colloids, and (3) the growth of silica colloids by deposition of silicic acid on colloid surfaces.

The rate of SiO_2 precipitation is strongly dependent on pH. Below pH 3 it appears to be catalyzed by H^+ .⁸ At higher pH values, the rate depends on OH^- .^{4,8}

In addition to forming colloids, silica will also deposit on surfaces. In sludge processing, any surface, including sludge solids, would be susceptible to silica deposition. Furlong et al.⁹ concluded that for oxides, an equilibrium concentration of $\sim 10^{-5} M$ (0.6 ppm as SiO_2) will ensure that all colloid surfaces will behave as silica surfaces. All unsoluble metal oxides are receptive to silica deposition. Iler noted that a silica film 20–30 Å thick on nickel powder rendered the metal insoluble in acid.⁴ Whether silica deposits on surfaces, forms colloids and gels, or does both depends on the degree of supersaturation, on the surfaces, and on solution conditions such as pH and the presence of other solutes.

The concentration of silica in leachates and wash solutions must be kept quite low, <100 ppm, to prevent the formation of silica gel. This could be done in two ways. The liquid-to-sludge ratio in acid treatment could be maintained at a level that ensures that only very dilute silica solutions would occur. Alternatively, a combination of nitric acid and hydrofluoric acid could result in silicon in solution as SiF_6^{-2} , rather than as SiO_2 . However, fluoride in solution may complex metal ions and cause a potential problem in the transuranic extraction (TRUEX) process.

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Appendix

FOUR TYPES OF SOLIDS FORMATIONS IN HANFORD SLUDGE PROCESSING

COAGULATION

Cell #	Sample ID	Tank ID	Sample Description	Image Attached (Yes or No)
164	1bw2451r3b1	T-104	First wash	Yes
165	1bw2451r3b2	T-104	Second wash	No
166	1bw2451r3b3	T-104	Third wash	Yes
173	1bw2451r3d	T-104	Combined leach and wash	Yes
177		T-104	Hanford procedure, prewash	No

LIGHT PRECIPITATION

Cell #	Sample ID	Tank ID	Sample Description	Image Attached (Yes or No)
168	1bw24t1r3c	T-104	Combined washes	No
182	2aw5t1r2a	B-202	1 M Nitric, 75°C	No
197	c-105L	C-105	Base leach	No
199	9bw51a	SX-113	Base leach	Yes
sx113c	sx113c	SX-113	Combined leach and wash	Yes

HEAVY PRECIPITATION

Cell #	Sample ID	Tank ID	Sample Description	Image Attached (Yes or No)
163	1bw24t1r3a	T-104	3.75 M NaOH, leach	Yes
178		T-104	Hanford procedure, first leach	Yes

GEL

Cell #	Sample ID	Tank ID	Sample Description	Image Attached (Yes or No)
169	1bw2451/0r3b1	T-104	First wash, t1/0 base leach	No
179		T-104	Hanford procedure, second leach	Yes
180		T-104	Hanford procedure, combined wash	Yes
181	2aw5t0r2a	B-202	Acid wash, room temperature	Yes
198	c-105L	C-105	Base leach	Yes
200	8bwt1a	C-108	Base leach	Yes
211	c-107L	C-107	Base leach	Yes

164

COAGULATION

166

COAGULATION

173

COAGULATION

199 **Suspended Particulates**

sx-113

Suspended Particulates

COATING

CRYSTALS

178

COATING

CRYSTALS

163

179

Gel Deposits & Crystals

180

Gel & Crystals

198

GEL DEPOSITS

181

Red Particles Gel Deposits

200

CLEAR GEL

211

CLEAR GEL

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